ESR spectra of PF2 and SF3 radicals

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Isotropic ESR Spectra of Fluorine-Containing Radicals in SF6 Matrices
Several years ago two of the present authors reported almost simultaneously the detection and identification of the radical PF$_2$ by ESR spectroscopy. Fessenden and Schuler$^1$ detected the radical during irradiation at $-135\, ^\circ \text{C}$ of nominally pure SF$_6$ with 2.8 MeV electrons, and found its spectrum to be considerably enhanced by the addition of small quantities of PF$_3$. Wan, Morton, and Bernstein,$^5$ on the other hand, detected the radical in $\gamma$-irradiated ND$_4$PF$_2$. The parameters describing this latter spectrum were $g=2.0108\pm0.0002$, $a_p=36.0\pm0.5$ G, and $a_y=60.5\pm0.5$ G. In 1970, Wei, Current, and Gendell$^3$ also claimed to have observed the ESR spectrum of PF$_2$ formed by the thermal decomposition and photolysis of P$_2$F$_4$ and PF$_3$H. In spite of discrepancies in the $g$ values, there was no suggestion that the earlier work$^{12}$ was suspect until Nelson, Jackel, and Gordy$^4$ obtained an isotropic spectrum of PF$_2$ by $\gamma$ irradiation of PF$_3$ trapped in a xenon matrix. Their parameters were quite different from those of preceding workers, $g=2.0020$, $a_p=84.6$ G, and $a_y=32.5$ G.

In order to resolve the issue we have sought new and unequivocal methods of preparing the radical PF$_2$: (a) The irradiation of 5 mole% PF$_3$ in a CF$_2$F$_2$ matrix with 2.8 MeV electrons$^{5,6}$ and (b) The UV photolysis of PF$_3$Cl in the liquid phase.$^7$ Both of these methods were successful, and yielded ESR spectra of PF$_2$ whose parameters (Table I) were consistent with those of Nelson, Jackel, and Gordy. Unfortunately our$^{13}$ previous identifications of the radical appear to have been incorrect. It would appear that Wei, Current, and Gendell$^3$ had also detected PF$_2$, although it was probably frozen into the matrix. Specifically, we feel that their "perpendicular" features might well be due to freely rotating radicals, suggesting the following isotropic parameters for PF$_2$ in an argon matrix, $g=1.9922$, $a_p=83.0$ G, and $a_y=33.5$ G.

Wan, Morton, and Bernstein's radical is almost certainly PO$_2$F$_2$. It has already been shown$^4$ that NH$_4$PO$_2$F$_2$ is susceptible to hydrolysis, and doubtless some conversion to ND$_3$PO$_2$F$_2$ occurred during the deuteration procedure. Furthermore, Begum, Subramanian, and Symons$^8$ have reported parameters for PO$_2$F$_2$ ($g=2.0100$, $a_p=43.8$ G, and $a_y=52.5$ G) which are similar to those of the radical detected$^6$ in irradiated ND$_3$PF$_6$.

The radical labelled PF$_2$ by Fessenden and Schuler$^1$ must also be reidentified. Since its spectrum can be observed when pure$^{10}$ SF$_6$ is irradiated, it must arise from a sulfur-centered radical, now believed to be SF$_3$. The spectrum of SF$_3$ is considerably enhanced by certain additives, notably PF$_3$. For example, the intensity of the published spectrum$^1$ (1% PF$_3$ in SF$_6$) is approximately ten times stronger (relative to that$^{11}$ of SF$_3$) than that observed in irradiated pure SF$_6$. The PF$_3$ seems either to participate in reactions involving SF$_3$ or to modify the matrix to make stabilization of SF$_3$ more likely.

The radical SF$_3$ is the prototype of certain sulfanyl radicals which have recently been studied.$^{12}$ These radicals, of the general type $(R_2O)S$, where $R_2=CF_3$ or SF$_3$, possess two equivalent ligands whose $^{19}$F hyperfine interactions exceed those of the unique ligand. In other words these derivatives of SF$_3$ do not possess a threefold axis, but a plane of symmetry. Consequently one would also expect SF$_3$ to exhibit a spectrum showing hyperfine interactions with two equivalent $^{19}$F nuclei, and a somewhat smaller interaction with a unique $^{19}$F nucleus. The parameters in Table II a, which were obtained from the aforementioned spectrum, accord very well with these deductions.

We have also succeeded in observing the spectrum of SF$_3$ in the liquid phase, by photolyzing a solution$^{13}$ of H$_2$S or D$_2$S and CF$_3$OF in Freon 13 at $-110\, ^\circ \text{C}$. The spectrum of SF$_3$, whose parameters appear in Table II b, persisted for only a few minutes. It is curious to note that the hyperfine interaction of the two equivalent $^{13}$F nuclei is slightly less in solution than in an SF$_3$ matrix, presumably the result of a slight change in the radical geometry.

### Table I. ESR parameters of PF$_2$ in (a) CF$_2$F$_2$ matrix at $-140\, ^\circ \text{C}$ and (b) in PF$_3$Cl dissolved in Freon 13 at $-100\, ^\circ \text{C}$.

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>$1.9994\pm0.0003$</td>
</tr>
<tr>
<td>$a_p$</td>
<td>$81.3\pm0.2$ G</td>
</tr>
<tr>
<td>$a_y$</td>
<td>$32.1\pm0.2$ G</td>
</tr>
</tbody>
</table>

### Table II. ESR parameters of SF$_3$ in (a) SF$_3$ matrix at $-135\, ^\circ \text{C}$ and (b) Freon 13 at $-110\, ^\circ \text{C}$.

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>$2.0054\pm0.0001$</td>
</tr>
<tr>
<td>$a_p$ (one nucleus)</td>
<td>$40.4\pm0.1$ G</td>
</tr>
<tr>
<td>$a_p$ (two nuclei)</td>
<td>$54.3\pm0.1$ G</td>
</tr>
</tbody>
</table>
Letters to the Editor

*NRCC No. 14127.
†Work supported, in part, by the U. S. Atomic Energy Commission.
‡NRCC Postdoctoral Fellow 1974.
5The experimental technique was similar to that described in Ref. 1. Solid C₂F₆ (m. p. −94°C) allows free rotation of small radicals down to about −165°C as shown by the isotropic spectra observed for CF₃ and C₂F₅ in this matrix (R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965) and in Advances in Radiation Chemistry, edited by M. Burton and J. L. Magee (Wiley-Interscience, New York, 1970), Vol. 2, p. 90.

6In addition to the ESR lines of PF₂ there were lines of PF₄ (the same spectrum as in SF₆) and weak lines of C₂F₅.

11Mass spectroscopic analysis of the SF₆ used in that work shows CF₄ to be the only significant impurity (~1%) and that PF₃ cannot be present to over about 0.01 mole%.
12This spectrum was originally assigned by Fessenden and Schuler to SF₆. See J. R. Morton and K. F. Preston, Chem. Phys. Lett. 18, 98 (1973) for the present assignment.
14100µl each of liquid H₂S and CF₃OF, separated by 100µl of Freon 13, were allowed to warm up to −96°C. If the sample did not explode, the spectrum of SF₃ could be detected upon photolysis at −110°C.